Sustainable biochar catalyst synergized with copper heteroatoms and CO_2 for singlet oxygenation and electron transfer routes

Zhonghao Wan[1], Yuqing Sun[1], Daniel C.W. Tsang[1,*], Iris K.M. Yu[1,2], Jiajun Fan[2], James H. Clark[2], Yaoyu Zhou[1,3], Xinde Cao[4], Bin Gao[5], Yong Sik Ok[6]

[1] *Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China*

[2] *Green Chemistry Centre of Excellence, Department of Chemistry, The University of York, York YO10 5DD, UK*

[3] *Hunan International Scientific and Technological Cooperation Base of Agricultural Typical Pollution Remediation and Wetland Protection, College of Resources and Environment, Hunan Agricultural University, Changsha 410128, China*

[4] *School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

[5] *Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States*

[6] *Korea Biochar Research Centre & Division of Environmental Science and Ecological Engineering, Korea University, Seoul, South Korea*

* Corresponding author email: dan.tsang@polyu.edu.hk

Abstract

We have developed a wood waste-derived biochar as a sustainable graphitic carbon catalyst for environmental remediation through catalytic pyrolysis under the synergistic effects between Cu heteroatoms and CO_2, which for the first time are found to significantly enhance the oxygen functionalities, defective sites, and highly ordered sp^2-hybridized carbon matrix. The copper-doped graphitic biochars (Cu-GBCs) were further characterized by XRD, FTIR, Raman, XPS, *etc.*, revealing that the modified specific surface area, pore structure, graphitization, and active sites (*i.e.,* defective sites and ketonic group) on the Cu-GBCs corresponded to the synergistic Cu species loading and Cu-induced carbon-matrix reformation under CO_2 environment during pyrolysis. The catalytic ability of the Cu-GBCs was evaluated using the ubiquitous peroxydisulfate (PDS) activation system for the removal of various organic contaminants (*i.e.*, Rhodamine B, phenol, bisphenol A, and 4-chlorophenol), and gave the highest degradation rate of 0.0312 min^{-1} in comparison with those of pristine GBCs and N_2-pyrolyzed Cu-GBCs ranging from 0.0056 to 0.0094 min^{-1}. The synergistic effects were attributed to the encapsulated Cu heteroatoms, evolved ketonic groups, and abundant unconfined π electrons within the carbon lattice. According to scavenger experiments, ESR analysis, and the two-chamber experiments, selective and sustainable non-radical pathways (*i.e.*, singlet oxygenation and electron transfer) mediated by Cu-induced metastable surface complex were achieved in the Cu-GBC/PDS system. This study offers the first insights into the efficacy, sustainability, and mechanistic roles of Cu-GBCs as an emerging carbon-based catalyst for green environmental remediation.

Keywords: engineered biochar; heteroatoms doping; metal-carbon composite; non-radical activation; sustainable waste management; green and sustainable remediation.

1. Introduction

Biochar has been extensively explored in agricultural and environmental applications,[1] such as soil amendment and contaminant stabilization,[2-5] carbon sequestration,[6-8] water/wastewater treatment,[9-14] and catalytic biomass conversion.[1, 15-17] It can be derived from various biomass wastes as renewable resources of high abundance, which favours the large-scale and economical production to satisfy sustainable development and circular bio-economy.[17-19] The versatile physicochemical properties of biochar are primarily determined by its intrinsic atomic arrangement of a carbon matrix, structural defective sites, pore structure, and surface functional groups.[18, 20, 21] To date, engineered metal-biochar composites with desirable physicochemical properties have been fabricated by introducing various multivalent transition metal components (Fe^0,[13, 22, 23] Fe_3O_4,[24-26] and Co,[27, 28] *etc.*) into the carbon lattice to evolve versatile active sites. Despite the high efficiency, the application of active multivalent transition metal-functionalized biochars unavoidably cause metal leaching into the environment, which is potentially hazardous to aquatic life and detrimental to clean water supply.[29, 30] For green environmental remediation, it is imperative to devise a transition metal-biochar composite with low toxicity and exhibiting excellent adsorptive capability and potential catalytic activity.

In this study, Cu was employed as the metal heteroatom for its inherent catalytic capacity and low toxicity,[31] while the lignin-rich wood waste was adopted as the feedstock with macro-/meso-pores for housing Cu species. In contrast with the commonly used transition metal catalyst, such as Co and TiO_2 that are precious metal facing an increasing threat of depletion,[27, 28, 32] the use of the low-cost Cu in our study appears to be more sustainable. Recent studies have revealed that a CO_2 medium could create surface defects and oxygen-containing functional groups that significantly enhanced the catalytic performance of biochar-supported materials.[24, 27, 28, 33, 34] The catalytic reforming of carbon matrix and the potential interactions with copper heteroatoms during CO_2 pyrolysis are yet to be revealed, particularly for the

physicochemical properties, surface structure, and interfacial chemical behaviour of the resulting Cu-biochar composites for catalytic applications.

The heterogeneous peroxydisulfate (PDS, $S_2O_8^{2-}$) activation system has been widely employed on engineered biochar. As an emerging green oxyanion, PDS can be directly activated by external energy input (heat, ultraviolet light, and ultrasound, *etc.*) or various metal-based catalysts to generate robust sulfate radicals ($SO_4^{\bullet-}$), which exhibit higher redox potential (E^0 = 2.5–3.1 V) and longer half-life period ($t_{1/2}$ = 30–40 μs) than $^{\bullet}OH$ (E^0 = 1.9–2.7 V, $t_{1/2}$ = 3–10 μs) over a wide range of pH values (pH = 2–8).[35,36] Organics degradation *via* radical pathways often requires intensive energy or chemical input that would limit its field application, and the generated radicals would demonstrate non-selective oxidation capability (*e.g.*, self-scavenging effects and highly chlorinated byproducts),[31,37] wherein the induced cannibalistic surface oxidation reaction would irreversibly alter the framework of carbon supports.[38] Thus, PDS activation *via* a more sustainable pathway is highly desirable. Zhang et al. reported that copper species could activate PDS to degrade chlorophenols *via* a non-radical pathway by forming a metastable complex on its surface.[31] Zhu et al. found that crystallographic manganese oxide could activate PDS to generate singlet oxygen (O_2^1) other than commonly reported free radicals (*e.g.*, $^{\bullet}OH$, $SO_4^{\bullet-}$, and $O_2^{\bullet-}$) for the degradation of aqueous contaminants.[39] In addition, various carbonaceous materials (*e.g.*, activated carbon, carbon nanotube, and graphene oxide (GO)) are capable of catalysing PDS for organic degradation *via* electron transition through graphitic matrix, which potentially are even more efficient than transition metal oxides (*e.g.*, Fe_3O_4, Co_3O_4, and α-MnO_2).[40] This superior performance could be ascribed to the well-defined sp^2-hybridized carbon matrix with versatile catalytic centre (*e.g.,* defects and ketonic groups) and abundant unconfined π-electrons.[20,41-43] In a recent study, graphitic biochar (GBC, pyrolyzed over 700 °C) with large specific surface area (SSA), ordered sp^2-hybridized structure, and tuneable defect sites as redox centre facilitated catalytic degradation.[44] Thus, it is hypothesized and then proven in this study that the introduction of

low-toxicity copper heteroatoms into the graphitic biochar matrix can enable the complimentary coupling of the catalytic centre and graphitic matrix of carbonaceous materials. This technique is more economic, scalable, and sustainable for green remediation applications *via* the non-radical PDS activation route.

In this study, Cu-doped GBC composites were synthesized through a one-step pyrolysis of $CuCl_2$-pretreated wood waste at 900 °C with continuous CO_2 purging as the reactive medium (in comparison to N_2 purging). The objectives of this research were to: (i) articulate the interactions of CO_2 medium and doped copper heteroatoms for tailoring the physicochemical properties, surface structure, and interfacial chemical behaviour of the resultant Cu-GBC composites, and (ii) capitalize on the evolution of sustainable pathways for non-radical PDS activation and catalytic degradation of various organic contaminants (*i.e.*, Rhodamine B (RB), phenol (PN), bisphenol A (BPA), and 4-chlorophenol (4-CH)). The results of this study are conducive to improving the future design of high-efficiency, engineered metal-biochar composites as green catalysts.

2. Experimental

2.1. Materials and chemical reagents

Apple-tree wood waste (collected from Guiyang city, Guizhou province, China) was selected as the feedstock of waste biomass. All the chemicals were of analytical reagent grade and solvents were of high-performance liquid chromatography (HPLC) grade. Ultrapure water (UW, 18.2 MΩ cm^{-1}) obtained from a Millipore Milli-Q Water Purification System (Milford, USA) was used for all experimental solutions.

2.2. Preparation of Cu-GBC composites

Before use, wood waste was cut into small pieces (< 5 cm), washed with ultrapure water (UW) for several times, oven dried at 80 °C overnight, then crushed by a high-speed rotary pulverizer, and finally sieved through a 120-mesh (particle size < 0.125 mm). The suspension of biomass with Cu^{2+} was prepared

by mixing 20 g wood with predetermined amounts of $CuCl_2$•$6H_2O$ in 1 L UW in a glass beaker, which was then agitated at 350 rpm for 24 h with a magnetic stirrer to maintain a uniform concentration. After water removal under continuous stirring at 80 °C for 12 h in a thermostat water bath, the slurry was completely dried in an oven at 80 °C for 24 h and then was sieved again for homogeneity. Next, the samples were placed in a tubular furnace with a medium heating rate of 5 °C min^{-1} to reach desired 900 °C, and the peak temperature was maintained for 2 h under CO_2 or N_2 purging at 500 mL min^{-1}.[44] After cooling down to room temperature inside the furnace, the stabilized samples were collected and rinsed with UW and alcohol for three times, respectively. After oven-drying overnight, the samples were ground and passed through a 200-mesh sieve (particle size < 0.075 mm). This particle size was smaller than the 120-mesh sieve used for biomass before pyrolysis, for the purpose of preparing biochars with reproducible quality and homogeneity, *i.e.,* uniform chemical impregnation and even heat distribution. For comparison, the pristine biochar was prepared following the above procedure, except for the use of $CuCl_2$-free UW for the suspension of wood waste. All prepared samples were stored in an airtight container for further use. The obtained products are denoted as Cu-GBCXC or Cu-GBCXN, where the X (5, 10, and 20%) and C/N represent the copper calculated mass ratio after wet digestion (Cu/BC, wt.%) and the selected purging gas (*i.e.*, CO_2 or N_2) during pyrolysis, respectively. Concerns over the toxicity of $CuCl_2$ are mitigated as the chloride ions evaporate during pyrolysis at 900 °C followed by absorption in NaOH solution (5 wt.%), while copper is retained on the carbon support. Nevertheless, life-cycle assessment is needed in the future to validate the net environmental benefits of Cu-GBC compared to conventional options.

2.3. Microscopic characterization of Cu-GBC composites

The characteristics of the GBC and Cu-GBC composites were determined *via* employing the Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) porosity, high resolution transmission electron microscopy (HRTEM), scanning electron microscopy-energy dispersive X-ray

spectroscopy (SEM-EDX), X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Detailed information on the characterization methods is available in the Supporting Information.

2.4. Catalytic degradation of various organic contaminants by Cu-GBC composites

The organic removal experiments were performed at 25 ± 1 °C under intensive mixing by a thermostatic oscillator (180 rpm). The solution pH was adjusted to 5.8 ± 0.2 using 0.1 M NaOH or HNO_3. To investigate the removal kinetics of various organic contaminants (*i.e.*, RB, PH, BPA, and 4-CH) by Cu-GBC composites, 0.3 g L^{-1} suspensions of Cu-GBC composites and 2 mM PDS (determined according to preliminary results) were added into 100 mL UW containing 0.1 mM organic contaminants in 250-mL conical flasks, while a similar reaction with GBC was also conducted for comparison. The commercial metal and metal-free catalysts (Fe_3O_4, Fe_2O_3, zero valent iron (ZVI), CuO, CoO, MnO_2, ZnO, and GO) were also evaluated for PDS activation. At predetermined time interval for sampling, aliquot sample of 1 mL was extracted from the conical flask to a glass vial and ethyl alcohol (EtOH) was added in excess for quenching. Same batch experiments quenching with sodium nitrite ($NaNO_2$) were also conducted to differentiate the contribution of adsorption and catalytic degradation. Then, the sample was filtered through a 0.45-μm pore-size polytetrafluoroethylene (PTFE) membrane (Millipore, USA) and analysed for the organic concentration. After the reaction, the Cu-GBC suspension was centrifuged, and the catalyst was collected and recovered by acetone (solid/acetone, 1:158, wt.%), which can effectively remove residual organics from the catalyst surface without altering its properties, according to our preliminary experiments (Supporting Information).

The scavenging experiments were performed to illustrate the contribution of different reactive oxygen species (*i.e.*, $^{\bullet}OH$, $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and O_2^1) by using 4 M EtOH (for $^{\bullet}OH$ and $SO_4^{\bullet-}$), 0.5 M tert-butanol (TBA) (for $^{\bullet}OH$), 0.05 M chloroform (CF) (for $O_2^{\bullet-}$), and 0.01 M furfuryl alcohol (FFA) (for O_2^1), respectively.[29]

Potassium iodide (KI, 10 mM) and pure acetone were chosen as inhibitors of non-radical pathway to suppress the surface-bound reactive species formation and direct contact between organic contaminants and carbon matrix, respectively.[44] Similar experiments (without the PDS addition) using the composites pre-treated by excess PDS (1 M) were performed to identify the contribution of organic removal *via* metastable complex.[45] The metal-free GBC (treated with ethylene-diamine-tetraacetic acid (EDTA)) and phenol-free GBC (treated with glycerol) were also employed (Supporting Information).[26] To identify the direct electron-transfer process during PDS activation, a two-chamber reactor separated by proton exchange membrane (PEM), equipped with carbon fibre electrodes, connected *via* electric wire, and loaded with Cu-GBC composite as an activator was prepared to separate organic contaminants from PDS (Supporting Information).

2.5. Analytical methods

The concentrations of organic pollutants were analysed by an UV-Vis spectrophotometer at a wavelength of 554 nm (UV-1100, China, limit of detection (LOD) of 0.1 mg L^{-1}) or a high-performance liquid chromatography (HPLC, Hitachi, Japan, LOD of 0.1 mg L^{-1}). The total organic carbon (TOC) was measured with a TOC analyser (SSM-5000A, Japan, LOD of 0.1 mg L^{-1}). The PDS concentration was determined by another UV-Vis spectrophotometer coupled with a computational platform (Optizen Pop, South Korea, LOD of 0.1 mg L^{-1}). The metal concentration was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific, USA, LOD of 0.1 μg L^{-1}). The electron spin resonance (ESR) spectra were obtained using an EMX10/12 spectrometer (Bruker, Germany). The solution pH was measured by a digital pH meter (Thermo 911600, USA). Detailed information on the analytical methods is available in the Supporting Information. Calibration of standard organic/inorganic concentrations was carried out prior to each analysis. Standards were analysed every 10 samples for quality assurance and

quality control. All experiments were performed in triplicate, and the results are presented as mean ± standard deviations.

3. Results and discussion

3.1. Physiochemical properties and crystalline structure of Cu-GBC composites

Selected physiochemical properties of GBC and the synthesized Cu-GBC composites with different Cu loadings (5–20 wt.%) under N_2 or CO_2 environment are summarized in Table 1. After wet digestion, the total Cu content in the Cu-GBC composites was shown to range from 3.8 ± 1.1 to 23.2 ± 5.5 wt.%. The HR-TEM images are shown in Fig. 1a-f. Homogeneous distribution of copper nanoparticles can be observed (Fig. 1b) with a lattice spacing of 0.223 nm assigned to the (111) plane of metal copper (Fig. 1d). These results suggest that copper was successfully reduced and loaded within the biochar framework after impregnation and pyrolysis processes. The specific surface area (SSA) and total pore volume of metal-free GBC fabricated in a CO_2 environment (358 m^2 g^{-1} and 0.323 cm^3 g^{-1}) were significantly higher than that generated in a N_2 environment (68.3 m^2 g^{-1} and 0.0516 cm^3 g^{-1}). The CO_2 medium promoted the formation of both micropores (219 m^2 g^{-1}) and meso/macro-pores (139 m^2 g^{-1}), as a result of intensive carbon reforming *via* Boudouard reaction ($C + CO_2 \rightarrow 2CO$) taking place at ≥ 710 °C.[24,33,34] The use of CO_2 may also react with the pore-blocking condensable hydrocarbons (*e.g.*, volatile organic compounds and tars), which could be converted into gaseous products to free the blocked pores and/or create new ones.[30,46] The SSA increased from 358 m^2 g^{-1} for the control CO_2-GBC to 388 m^2 g^{-1} and 468 m^2 g^{-1} for the Cu-GBC5C and Cu-GBC10C, respectively, indicating that $CuCl_2$ acted as a pore-forming agent. The external surface area and micropore volume also increased from 139 to 175 m^2 g^{-1} and 0.121 to 0.156 cm^3 g^{-1} (*i.e.* 39.2–53.1% of total pore volume), respectively, suggesting the more significant formation of both

mesopores (2−50 nm) and micropores (< 2 nm) in Cu-GBC10C framework, which are also displayed in the HR-TEM image (Fig. 1e). Thus, the Cu-induced catalytic graphitization of carbon matrix during pyrolysis could possibly generate more zero-dimensional point defects (*i.e.*, vacancy and edge sites) and three-dimensional volume defects (*i.e.*, lattice disorder and void).[46] However, excessive Cu loading caused a sharp decrease in SSA (4.89 m^2 g^{-1}) for the Cu-GBC20C, which might result from the pore blockage after Cu precipitation. As shown in Fig. 2a & S1, N_2 adsorption curves of all the composites exhibited the typical type-IV adsorption/desorption isotherms with H4-type hysteresis loop at medium relative pressure (P/P_0 = 0.45–0.95), which further demonstrated the existence of micropores and mesopores derived from capillary condensation,[47] corresponding to the average pore size data of GBC and Cu-GBC composites in Table 1.

Compared with the control CO_2-GBC, the pH of the Cu-GBC composites decreased from 10.5 to 10.3–8.51, which is attributed to the hydrolysis of Cu^{2+} and/or the generation of acidic functional groups (*e.g.,* phenolic and carboxylic groups).[48] The pH value at the point of zero charge (pH_{pzc}) increased after copper encapsulation (Fig. S2) owing to an increasing positive surface charge after the incorporation of copper atoms, which is expected to tailor the electronic states of the adjacent carbon *via* charge transport to modulate the electron density.[40] The SEM-EDX analysis of the GBC and Cu-GBC composites are presented in Figs. S3-S5. In contrast to the relative smooth surface with multilayer structure on the N_2-GBC (Fig.S3a-b), porous channels and more mesopores were observed on the surface of CO_2-GBC (Fig.S3c-d). With respect to Cu-GBC5C, Cu particles were mainly incorporated in the interior micropores of the flaky cracking GBC surface (Fig. S3e). As the Cu loading increased, *i.e.*, for Cu-GBC10C, Cu particles with diameters ranging from micro- to nano-scale became evident (Fig. S4c-d). These particles were evenly distributed in the pores and on the surfaces of bulkier dendritic flocs, up to a particle size of 400–500 nm. In contrast, obvious particle aggregation into discrete spheres of ~10 μm was observed in the Cu-GBC20C (Fig. S3f). These findings are consistent with the variation in surface area and pore size distribution of the

222 Cu-GBC composites (Table 1). EDX analysis (Fig. S5) revealed the co-existence of Cu, O, C, Ca, Mg, and
223 P elements on the Cu-GBC10C surfaces. The significantly higher oxygen content (21.1 wt.%) of
224 Cu-GBC10C compared with that of the Cu-GBC10N (1.83 wt.%) indicated that more oxygen could be
225 introduced into the carbon matrix under CO_2 medium. Enriched oxygen-containing functionalities may act
226 as the anchoring sites for the impregnation of Cu species (Table 1).[49] Besides, the induced edges terminated
227 with hydrogen and oxygen atoms on the sp^2-hybridized carbon were reported to possess high affinity to
228 adsorb oxyanions.[20, 50]

229 The XRD patterns of the GBC and Cu-GBC composites are shown in Fig. 2b. In the case of the N_2-GBC,
230 the carbon matrix demonstrated a broad peak at 2θ value of 20–25°, which can be assigned to graphite
231 corresponding to the amorphous plane of (002) in carbonaceous materials.[51] Nonetheless, the spectra of the
232 CO_2-GBC presented the characteristic peaks at 29.41°, 35.93°, 39.42°, 47.14°, and 47.42° corresponding to
233 the (104), (110), (113), (024), and (018) planes of calcite, respectively, as typical ash component of wood
234 waste.[52, 53] As for the Cu-GBC composites, the characteristic peaks at 35.04°, 38.48°, and 50.43° were
235 assigned to the (002), (111), and (112) planes of CuO,[54, 55] while the peaks at 43.29° and 74.13°
236 corresponded to the (111) and (220) planes of Cu^0,[56] respectively. In particular, in contrast with the
237 N_2-pyrolysis, the CO_2 environment suppressed the crystalline sizes of CuO (0.61 *vs.* 0.89 nm) and Cu^0 (1.97
238 *vs.* 2.28 nm) particles, based on the calculation using the Scherrer equation.[45] Thus, copper heteroatoms can
239 be successfully grafted in the framework of biochar, and hence likely to significantly increase its catalytic
240 reactivity by forming Lewis acid-base adduct (*i.e.,* reversibly donate and accept electrons)[57, 58] or surface
241 metastable complex (*i.e.,* non-radical pathway).[31] The absence of a calcite peak in the Cu-GBC XRD
242 pattern suggests that the doped copper heteroatoms saturated the exchangeable sites that originally held
243 Ca.[13]

The Raman spectra of the GBC and Cu-GBC composites further elucidated the physical characteristics of the carbonaceous materials, as shown in Figs. 2c & S6. The two peaks at 1310 and 1590 cm^{-1} correspond to the characteristic D and G bands of carbon, *i.e.,* defects of sp^3 C and in-plane vibrations of sp^2 C in curved graphitized carbon sheet.[42, 59] In all samples, the Raman spectra were deconvoluted into eight characteristic peaks that were assigned to sp^2 C–H of aromatic rings (S^1) at 1060 cm^{-1}, $C_{aromatic}$–C_{alkyl} (S) at 1185 cm^{-1}, Aryl-alkyl ether (S^2) at 1230 cm^{-1}, defect bands and small ordered fused benzene rings (D) at 1310 cm^{-1}, methyl group and amorphous carbon (V^1) at 1380 cm^{-1}, semicircle ring breathing (V) at 1465 cm^{-1}, aromatics with 3–5 rings (G^1) at 1540 cm^{-1}, and highly ordered sp^2 graphitic carbon (G) at 1590 cm^{-1}.[60, 61] The area ratios of the D peak to the G peak (A_D/A_G) and the sum of G, V, and V^1 peaks ($A_D/A_{(G1+V+V1)}$) of the CO_2-pyrolyzed composites are greater than that produced in N_2, suggesting that CO_2 medium induced more fused aromatic rings and structural edge defects within the biochar matrix during pyrolysis.[23, 62, 63] This can be attributed to the enhanced dehydrogenation of organic matter (*viz.* Boudouard reaction: $C + CO_2 \rightarrow 2CO$; biomass $\rightarrow$ biochar + tar + C_nH_m) at high temperature with CO_2 purging, which could generate more vacancy and zigzag edges as structural-dimensional defects.[46] The ratios of A_D/A_G and $A_D/A_{(G1+V+V1)}$ also increased with the increasing Cu loading (Fig. S6c-d), suggesting that $CuCl_2$ may promote the catalytic graphitization of biochar during the synthesis of the Cu-GBC composites, which accounted for more newly formed volume defects (*e.g.,* void).[64] Intriguingly, the Cu-GBC10C composite exhibited both a higher level of graphitization and defects than the lab-synthesized GO (Fig. S7b) prepared in our recent study,[49] which possibly account for the improved performance in the catalytic activation of PDS for organics degradation with abundant free-flowing π electrons and defective sites. Graphitic carbon clusters with a crystalline spacing of 0.25 nm (assigned to graphite) can be observed in the HR-TEM images of Cu-GBC10C (Fig. 1e-f), which further confirms the emergence of highly ordered graphitic nature after the introduction of copper heteroatoms.

3.2. Surface chemical behaviour and thermal stability of Cu-GBC composites

FTIR spectra helped to determine the functional groups on the surfaces of the GBC and Cu-GBC composites (Fig. 2d). In the case of the N_2-pyrolyzed composites, the broad spectral band with a weak peak at 3429 cm^{-1} was attributed to the presence of the O–H stretching vibration in alcoholic and phenolic –OH groups. The pyrolysis at 900 °C diminished most of the functional groups ubiquitously present in low-temperature biochars, because dehydration of cellulosic and ligneous components at high temperature (>700 °C) tend to decompose the majority of the aliphatic and phenolic organic compounds.[1,48,65] After Cu impregnation and pyrolysis in CO_2 environment, the band disappeared for –OH and C–H at 3429 and 835 cm^{-1}, respectively, whereas an aromatic C=O stretching vibration in conjugated ketones and quinones evolved at 1659 cm^{-1}.[66] This was indicative of catalytic reformation and condensation of carbon matrix during the synthesis of the Cu-GBC composites,[27,67] which may account for the greater graphitic carbon observed in the Raman spectra (Figs. 2c & S6). It should be noted that the produced ketonic group (C=O) is indispensable for the activation of PDS and the generation of singlet oxygenation for organics degradation.[20,41,44,68,69]

TGA was employed to verify the generation of ketonic group (C=O) during the aforementioned catalytic reformation. As shown in Fig. S17, the mass decay (TG) of raw wood waste exceeded 80% and the broad peak (*peak 1*) at 345.5 °C in derivative thermogravimetry (DTG) was consistent with the dehydration of cellulosic or ligneous components and the lignin/cellulose-derived transformation at mid-level pyrolytic temperature (200-550 °C).[48,65] The CO_2-pyrolyzed biochar composites exhibited greater mass decay than their N_2-pyrolyzed counterparts, especially for Cu-GBC10C (30.1%, compared to 17.1% of Cu-GBC10N). Both apparent peaks at 643.6 °C (*peak 2*) and 634.8 °C (*peak 3*) in the DTG curves for CO_2-GBC and Cu-GBC10C correspond to the decomposition of conjugated ketones (C=O),[65] suggesting that copper heteroatoms and CO_2 medium could synergistically increase the oxygen levels during the pyrolytic process.

The XPS data indicated that the GBC was composed of C 1s and O 1s, whereas the Cu-GBC composites comprised C 1s, O 1s, and Cu 2p. In all samples, the C 1s spectra consisted of five different peaks that were assigned to O=C–OH at 288.8 eV, C=O at 286.6 eV, C–O at 285.8 eV, C–C at 285.4 eV, and C=C at 284.8 eV, while the three fitted peaks of O 1s could be assigned to O–C=O at 533.6eV, O–C at 532.2 eV, and O=C at 530.8 eV, respectively.[70] As the Cu impregnated biomass was pyrolyzed under CO_2 purging, there was a significant increase in the content of O=C (from 17.7% to 41.1%) compared to CO_2-GBC (Fig. 3b & S8). This observation corroborates the transformation of O–C (532.2 eV) into O=C (530.8 eV) *via* Cu-induced catalytic oxidation process.[42] Duan et al. reported that oxygen functionalities can determine the inherent catalytic capability of carbonaceous materials, and both oxygen contents and species of oxygen groups should be carefully optimized.[20] In this research, copper heteroatoms are favourable to tune the oxygen groups by transforming more oxygen functionalities into ketonic C=O, which would contribute to the better catalytic performance of Cu-GBC10C in the subsequent section.

In addition, as shown in Figs. 3c & S10, CuO shake-up (943.8 eV) accounted for only 19.9% and slight increases were observed after reaction (from 19.9% to 20.6% for CuO, 27.8% to 36.3% for Cu^{2+}), which ruled out the electron donation or sole CuO-induced non-radical pathway as the primary reaction route. It has been reported that metal–O–C bond could give rise to denser local electronic states forming more reactive sites,[40] and similar synergy between Cu and graphitic carbon may explain the phenomenon in this work. This should be further verified *via* density functional theory calculations and X-ray absorption spectroscopy in the future. The current study evidences that the CO_2 environment and Cu doping promoted the formation of kenotic groups during pyrolysis,[13, 71, 72] and ultimately the sp^2-hybridized carbon framework was converted into an active state with the new accommodated copper heteroatoms and tuned oxygen functionalities.

3.3. Cu-GBC performance for PDS activation and catalytic degradation of organic contaminants

A typical rhodamine dye of RB was chosen as the target organic pollutant to evaluate the catalytic performance of synthesized composites for PDS activation and the kinetic data were fitted using a pseudo-first-order kinetics model.[31,39,73] The raw wood waste (5 g) was combusted in air to obtain its ash (0.48 g), which was found to barely activate PDS for RB degradation, indicating that the metal residues in the biomass do not contribute to the catalytic oxidation on GBCs. The adsorptive removals of RB were insignificant on GBCs and Cu-GBC10N, while PDS alone could not oxidize the dye (< 5%) without the addition of catalysts (Fig. S11). In contrast, Cu-GBC10C showed notable RB adsorption (~ 40%), possibly due to stronger interactions with the enriched oxygen functionalities on the biochar surface. The larger SSA (468 m^2 g^{-1}, Table 1) and higher graphitic level of Cu-GBC10C might also contribute to an improved adsorption capacity with stronger pore-filling adsorption and π-π interaction. However, Cu-GBC5C and Cu-GBC20C demonstrated unfavourable adsorptive performance due to insufficient SSA and active sites (data not shown). An 86.4% degradation rate of RB was achieved in the Cu-GBC10C/PDS system in 30 min, demonstrating a better degradation efficiency than most commercial heterogeneous catalysts (metal-based systems including CuO, ZVI, Fe_2O_3, Fe_3O_4, ZnO, CoO, and MnO_2), while an inferior degradation rate of 22.3% was obtained by Cu-GBC10N (Fig. 4a). In Fig. S12, compared to the pristine biochar (N_2-GBC, 0.0056 min^{-1} with 7.8% degradation removal; CO_2-GBC, 0.0071 min^{-1} with 15.6% degradation removal) and Cu-GBC10N (0.0094 min^{-1} with 22.3% degradation removal), Cu-GBC10C (0.03122 min^{-1} with 86.4% degradation removal) gave rise to a 5.6-, 4.5-, and 3.3-fold enhancement of the degradation rate as a result of the larger surface area, higher graphitization degree, and more active sites (*i.e.,* C=O in ketonic group). This phenomenon also evidences a synergism of the Cu catalytic reformation and CO_2 purging during biomass pyrolysis. Cu-GBC10C was chosen as the sustainable biochar catalyst for the subsequent comparative, kinetics, and mechanistic studies.

Fig. S13 shows that ~ 90% removals of RB, PN, and BPA at 0.1 mM could be rapidly achieved by Cu-GBC10C within 30 min. However, it was poor in 4-CH oxidation (39.8%). This lower performance probably indicates that organic pollutants (*e.g.,* RB, PN, and BPA) with lower ionization potential (IP) (IP = 7.4–8.5) were more prone to be oxidized by mild reactive oxygen species (ROSs) (*e.g.,* $^1O_2$) generated in Cu-GBC/PDS system *via* a non-radical pathway. Previous findings suggested that some highly-graphitic carbonaceous materials (CNTs and carbonized N-containing polymers, *etc.*) and metal oxides (CuO and β-MnO_2, *etc.*) tended to exhibit a higher selectivity towards electron-rich phenolic compounds.[31, 39, 41, 42] When the concentration of organics increased to 0.5–0.6 mM, 40.3% and 79.7% removals of RB and PN were obtained in 30 min, possibly limited by the insufficient active sites on Cu-GBC10C.

To affirm the rate-determining step of the reaction (at pH = 5.8 ± 0.2), the pseudo-first-order kinetics was employed to calculate the observed rate constant (k_{obs}) in the first 30 min at different catalyst loadings, PDS dosages, or organic concentrations. Increasing PDS concentration from 1 to 5 mM marginally improved k_{obs} (Fig. 5b). Catalyst loading (0.1−0.5 g L^{-1}) and initial RB concentration (0.05−0.6 mM) posed more significant impact on the removal rate constants (Fig. 5a&c). The curves between logarithms of k_{obs} and dosages of Cu-GBC10C, PDS, and RB were plotted accordingly, showing good linearity between ln(k_{obs}) with ln(Cu-GBC10C) (R^2 = 0.983), ln(PDS) (R^2 = 0.821), and ln(RB) (R^2 = 0.965) (Fig. 5d). In addition, the positive correlation (R^2 = 0.999) was established between the adsorbent dosage (g L^{-1}) and adsorptive removal rate (k_{obs}) (Fig. 5d). The slopes of ln(k_{obs}) against ln(Cu-GBC10C), ln(PDS), ln(RB), and ln(adsorbent) were estimated to be 0.968, 0.095, -0.653, and 0.860, respectively, which can be taken as the orders of reactivity in the overall organic removal rate. The lowest reaction order of PDS suggests that the active sites for PDS adsorption are limited, and self-scavenging effect or cannibalistic surface oxidation reaction could also be excluded accordingly, thus demonstrating the features of a typical non-radical activation.[38, 74] The higher reaction orders with respect to Cu-GBC10C, RB, and adsorbent concentrations

indicated that the adsorption of organic compounds on the Cu-doped GBC might be the rate-determining step for the non-radical oxidation.[31, 39, 44, 75]

3.4. Contribution of radical and non-radical pathways to PDS activation and organics degradation

In previous studies, it has been discovered that the persistent free radicals (PFRs) were formed from the decomposition of organic structure (*i.e.,* hydroquinone) in biochars derived at moderate temperatures (300−500 °C),[76] which served as the redox centres to deliver electrons to PDS to evolve sulfate radicals.[26] However, Ruan et al. revealed that pyrolysis of different biomass (*e.g.,* pinewood, rice husk, and cow manure) at temperature above 700 °C generally removed all PFRs due to the elimination of oxygen functionalities and condensation/graphitization of carbon clusters.[77] In this work, the removal rate of phenol-free GBC (Supporting Information) was comparable to GBC, indicating that PDS activation by PFRs on highly graphitic biochars for catalytic degradation can be ruled out.

More interestingly, the radical quenching tests (Fig. 6a and Table 2) indicate that the addition of free radical scavengers,[44, 57, 78, 79] *i.e.,* EtOH ($k_{SO_4^{\bullet-}}$ = (1.6−7.7) × 10^7 M^{-1} s^{-1}, $k_{\bullet OH}$ = (1.2−1.8) × 10^9 M^{-1} s^{-1}), TBA ($k_{SO_4^{\bullet-}}$ = (4.0−9.5) × 10^5 M^{-1} s^{-1}, $k_{\bullet OH}$ = (3.2−7.6) × 10^8 M^{-1} s^{-1}), and CF ($k_{O_2^{\bullet-}}$ = (1.1−3.2) × 10^9 M^{-1} s^{-1}) had an insignificant impact on organics removal with only a 3.2, 0.19, and 9.4% decrease in the removal efficiency, respectively. This implies that Cu-GBC10C/PDS is an oxidative system not relying on free radicals but non-radical pathways due to the absence of DMPO−SO_4 characteristic signal peaks (1:1:1:1:1:1, αN = 13.2 G, αH = 9.6 G, αH = 1.48 G), although DMPO−OH characteristic signal peaks (1:2:2:1, αH = αN = 14.9 G) were observed in the ESR spectra (Fig. 4c). The generation of hydroxyl radicals might result from the oxidation of adsorbed water on the graphitic biochar surface, which has been reported in dimensional-structured nanocarbon system.[20] However, the impact of radical quenching on the reaction rate was moderate with 31.7%, 9.1%, and 39.1% decline, respectively, indicating that the scavengers with

nonpolar properties might suppress the adsorption of RB on the hydrophobic surface of Cu-GBC10C, and this phenomenon corresponds to the adsorption of organic compounds as the rate-limiting step.

To further investigate the interfacial reaction, KI and pure acetone were employed to quench the direct surface contact between PDS/RB and the carbon matrix, respectively.[80, 81] The almost unaffected organic removal despite the excess KI (10 mM) addition suggests that the increase in ionic strength could not affect the strong interaction between Cu-GBC10C and PDS. The substantial inhibitory effect of pure acetone (0.00211 min^{-1} with 18.9% removal) further indicates that the surface adsorption of organics could be vital for the total oxidation,[44] suggesting that the degradation occurred within the carbon matrix rather than the bulk solution corroborating the non-radical feature.

Recent studies have reported that ketonic- and quinone-like moieties on graphitic carbon with strong nucleophilic nature and high electron density can catalyze PDS to produce $^1O_2$ under mild condition.[41, 44, 80] Thus, FFA ($k_{^1O_2}$ = 1.2×10^8 M^{-1} s^{-1}) was used to scavenge $^1O_2$ in the reaction. FFA (0.01 M) significantly reduced the RB removal efficiency to 50.0% (0.00593 min^{-1}) in 120 min, indicating that $^1O_2$ contributed to a large portion (nearly half) of the catalytic oxidation. A trapping agent of TEMP was used to detect the production of $^1O_2$ without light. A characteristic three-line signal of TEMPO adducts appeared (Fig. 4d, 1:1:1, α = 16.9 G), which can be assigned to the oxidation of TEMP by $^1O_2$. In contrast to other GBC composites, the intensities of TEMPO and DMPO−OH in Cu-GBC10C increased sharply, implying that Cu-GBC10C possessed the highest reactivity, which originated from the encapsulated copper heteroatoms and the evolved ketonic groups (C=O) on Cu-GBC10C, possibly at the edges of the carbon matrix.[81] Moreover, the PDS-pretreated Cu-GBC10C achieved an 8.15% RB degradation without the PDS addition, whereas those for the Cu-free CO_2-GBC and EDTA-pretreated Cu-GBC10C (2.12−2.31%) were negligible (Fig. S14). Thus, it can be inferred that C=O would induce the surface metastable complex between copper heteroatoms and PDS (*i.e.*, ≡Cu−$O_3SOOSO_3^-$ or ≡Cu^{II}−$O_3SOOSO_3^-$), which can readily accept electrons

403 from electron-rich phenolic compounds for $^1O_2$ generation,[68] and correspond to a significant peak shift at
404 531 nm in the UV-vis spectra of the Cu-GBC10C (Fig. 4b). This observation corroborates the C 1s spectra
405 that depict a lower C=O ratio (from 41.1% to 17.4%) for the Cu-GBC10C after PDS activation.

406 *3.5. PDS reduction and RB oxidation in two chambers separated by a proton exchange membrane*

407 As above, the experimental results proved a significant role of $^1O_2$ in PS activation *via* a non-radical
408 reaction pathway, whereas the RB removal pathway was not completely terminated in the presence of $^1O_2$
409 quenchers. Moreover, in the Cu-GBC mediated non-radical pathway, an electron-transfer process from
410 organics and donation of free-flowing π electrons by GBC to the activated surface metastable complexes *via*
411 the conductive surface of carbonaceous materials was expected, in view of the differences of inherent redox
412 potentials between organic pollutant and PDS molecules.[23] Thus, the electron-transfer non-radical pathway
413 was further identified by examining Cu-GBC10C-mediated electron transfer from organic substrates to
414 PDS using a PEM that physically partitioned the reaction system into two chambers containing PDS and
415 RB (Fig. 7). In this system, free electrons were transported from the anode to the cathode through the
416 connected wire. The Cu-GBC10C particles were homogeneously dispersed in the bulk solution under
417 vigorous shaking to achieve sufficient contact with the electrodes, *i.e.,* carbon fibre brushes with high SSA.
418 As a PEM with high water impermeability is likely to reject organic/inorganic impurities and ROSs (*e.g.,*
419 $^{\bullet}OH$ and $^1O_2$), simultaneous RB oxidation and PDS reduction in the physically separated chambers (*i.e.,*
420 anode and cathode) would be a strong evidence for the electron-transfer mechanism, in which Cu-GBC10C
421 mediates electron transfer from organics to PDS.

422 As shown in Fig. 7, increased amounts of reactants (5-fold catalyst and oxidant addition) were added in
423 the anode chamber (no oxidant) and cathode chamber (no pollutant), respectively. Control experiments were
424 conducted detaching the linking wire between the two electrodes, and the results indicated that RB
425 concentration in the cathode chamber declined to less than 5% in 360 min due to the adsorption by the

426 employed Cu-doped biochar, as approximately 10% PDS concentration decomposed simultaneously. The
427 PDS-saturated state of the catalyst was reached after 360 min. A continuous PDS decrease to 55.6 ± 3.1% in
428 4320 min could be achieved in a wire-connected group compared with the wire-detached control (90.8 ± 3.3%
429 in 4320 min), which confirmed that the PDS was activated without direct contact with pollutant. Neither
430 PDS nor RB was detected in the opposite side of PEM, thus the continuous PDS concentration decline in
431 the separated chambers proved our hypothesis that electron transfer pathway does not rely on ROSs. The
432 overall schematic diagram of the mechanistic routes (*i.e.*, singlet oxygenation and electron transfer) is
433 presented in Fig. 8.

434 *3.6. Effect of pH values and reusability/recyclability*

435 Fig. S15 presents the influence of initial solution pH values on the organics degradation (*i.e.,* RB and PN)
436 by the Cu-GBC10C. The performance of the Cu-GBC10C was highly pH-dependent and the degradation
437 of PN steadily decreased with pH increasing from 3.0 to 9.0. In the case of RB, efficiency rose with
438 increasing pH values from 3.0 to 5.8 followed by pronounced decrease in RB removal as the solution pH
439 was further elevated to 9. Fig. S15 displays the highest degradation efficiency of PN and RB as 82.1% and
440 86.4% at the solution pH values of 3.0 and 5.8, respectively. The obvious difference at various solution pH
441 values can be ascribed to the composite surface charge, organic speciation, and Cu dissolution. As illustrated
442 in Fig. S1, there was an obvious decrease in the zeta potential as the solution pH increased. At the solution
443 pH above 2.08, the zeta potential was negative and undesirable for the removal of
444 negatively-charged/deprotonated organics (RB-pK_a = 3.5 and PN-pK_a = 9.8).[82, 83] Meanwhile, the surface of
445 Cu-GBC10C became more negatively charged with the increase of solution pH, which was less conducive
446 to anionic PDS ($S_2O_8^{2-}$) forming a metastable complex.[84] In addition, an acidic environment at pH 3.0−6.0
447 adversely affected the organics degradation due to inevitable Cu dissolution from the Cu-GBC10C
448 (0.014−0.925 mg L^{-1}).

Reusability/recyclability is an important indicator evaluating the sustainability of Cu-GBC10C. The removal efficiency decreased from 95.8% to 30.6% after four cycles (Fig. S16), probably because the Cu nanoparticles were exhausted by chemical reduction and/or the degradation intermediates/products covered the active sites, and changed the surface chemistry and electron transfer. Nevertheless, the Cu-GBC10C could maintain 73.2% of the RB removal efficiency after four cycles *via* facile acetone regeneration process, suggesting that the Cu-GBC10C had a good reusability/recyclability and stability when the degradation intermediates were removed. It is noted that the trivial amount of leached Cu (Fig. S15) in bulk solution could not catalyze the degradation, because adsorption of target contaminants on Cu-GBC composite surface was evidenced to be necessary (Section 3.4) and chemical desorption of organic intermediates/products in acetone was required to recover the catalytic activity (Fig. S16). We herein propose the Cu-based and ketonic active sites on GBC as a sustainable alternative to the consumable catalytic sites in the conventional carbocatalysts. By using persulfate activation as a model reaction, our findings can foster wider applications of Cu-GBC composites in sustainable biorefinery,[85] soil amendment,[2, 86] stabilization/solidification,[87] *etc.*, where electron transfer routes can potentially take place. Future studies may also investigate the production of Cu-GBC from wood waste contaminated by Cu-containing preservatives, which will further benefit sustainable development and zero waste principles.

4. Conclusions

Through the integrated analysis of the surface characteristics and contaminant interactions, we demonstrated that the highly graphitic Cu-doped biochar fabricated in CO_2 environment manifested a superior catalytic performance of PDS activation for the degradation of various organic contaminants, out-performing most of popular and costly heterogeneous catalysts. Selective degradation routes *via* singlet oxygenation and mediated electron transfer were promoted by design and validated as the predominant

non-radical mechanisms. The organics adsorption was identified as the rate-determining step of the reaction. The scientific merits of this paper are highlighted as follows: (i) a new approach for utilizing waste biomass to synthesize value-added products with versatile metal-heteroatoms-induced active sites and high graphitization employing greenhouse gas CO_2; (ii) a highly reactive, selective, green, and stable method for catalytic degradation of organic contaminants with cost-effective and environmentally benign biochar composites; (iii) advanced mechanistic insights into the synergistic effects of the copper heteroatoms and CO_2 environment during metal-impregnated biomass pyrolysis and catalytic degradation. Therefore, the Cu-biochar composites are easily prepared and low-cost carbon-based catalysts suitable for green and sustainable remediation.

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